

## Polyelement substituted cyclopentadienes and indenenes – novel ligand precursors for organotransition metal chemistry<sup>1</sup>

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Received 10 July 1996; accepted 5 September 1996

### Abstract

A series of polyelement substituted cyclopentadienyl and indenyl boranes and arsanes containing Me<sub>3</sub>Si–, Me<sub>3</sub>Sn– was synthesised; (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)BX<sub>2</sub> (**2**, X = Cl; **3**, X = Br) and (C<sub>9</sub>H<sub>6</sub>SiMe<sub>3</sub>)BX<sub>2</sub> (**4**, X = Cl; **5**, X = Br) were obtained by Si/B exchange reaction in a low yield when X = Cl and in a moderate yield when X = Br, whereas Flu(SiMe<sub>3</sub>)<sub>2</sub> does not react with BBr<sub>3</sub> at all. PhB(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub> (**6**) and PhB[C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**7**) were synthesised using appropriate thallium cyclopentadienides in high yields, 81% and 99% respectively. More bulky indenyl derivatives TrsB(C<sub>9</sub>H<sub>7</sub>)<sub>2</sub> (**8**, Trs = (Me<sub>3</sub>Si)<sub>3</sub>C–), PhB(C<sub>9</sub>H<sub>6</sub>SiMe<sub>3</sub>)<sub>2</sub> (**9**), Ph<sub>2</sub>B(C<sub>9</sub>H<sub>6</sub>SiMe<sub>3</sub>) (**10**) were prepared by metathesis reactions of lithium indenides with boron halides in high yields. A subsequent transmetallation of C<sub>9</sub>H<sub>6</sub>(SnMe<sub>3</sub>)<sub>2</sub> with PhBCl<sub>2</sub> followed by addition of ZrCl<sub>4</sub> gave (η<sup>5</sup>-C<sub>9</sub>H<sub>6</sub>SnMe<sub>2</sub>Cl)<sub>2</sub>ZrCl<sub>2</sub> (**11**) in the form of one of two possible diastereomers in high yield. C<sub>9</sub>H<sub>6</sub>(SiMe<sub>3</sub>)SnMe<sub>3</sub> reacts with BCl<sub>3</sub> to give the appropriate bis-indenyl derivative, that was easily converted to the *ansa*-zirconocene complex [MeB(η<sup>5</sup>-C<sub>9</sub>H<sub>6</sub>)<sub>2</sub>]ZrCl<sub>2</sub> (**12**). The sterically demanding bis-indenyl ligand **8** underwent direct deprotonation by *t*-BuLi, affording [TrsB(η<sup>5</sup>-C<sub>9</sub>H<sub>6</sub>)<sub>2</sub>]ZrCl<sub>2</sub> (**13**) by in situ reaction with Me<sub>3</sub>SnCl and ZrCl<sub>4</sub>.

Indenylarsanes (C<sub>9</sub>H<sub>7</sub>)<sub>3</sub>As (**14**), *t*-BuAs(C<sub>9</sub>H<sub>7</sub>)<sub>2</sub> (**15**), C<sub>9</sub>H<sub>7</sub>AsMe<sub>2</sub> (**16**) and (C<sub>9</sub>H<sub>6</sub>SiMe<sub>3</sub>)AsMe<sub>2</sub> (**17**) were synthesised by reactions of lithium indenides with arsenic halides in good to excellent yields. All these compounds were characterized by analytical and spectroscopic data (NMR, MS). **14** and **15** exist as complex isomeric mixtures with the arsenic atom in the allylic position of the indenyl ring; the crystal structure of a *meso* form of **15** was determined by X-ray diffraction methods. **17** consists of two isomers with a vinylic (**17a**) and an allylic (**17b**) Me<sub>3</sub>Si substituent. Stannylation of **16** by Me<sub>3</sub>SnNEt<sub>2</sub> led exclusively to the diallylic derivative (C<sub>9</sub>H<sub>6</sub>AsMe<sub>2</sub>)SnMe<sub>3</sub> (**18**) in quantitative yield. The latter was readily converted to a polymeric, half-sandwich indenyl zirconocene [η<sup>5</sup>-(C<sub>9</sub>H<sub>6</sub>AsMe<sub>2</sub>)ZrCl<sub>3</sub>]<sub>n</sub> (**19**) in high yield. Further reaction of **19** with Cp\*Li resulted in the formation of a new arseno substituted bent metallocene complex [η<sup>5</sup>-(C<sub>9</sub>H<sub>6</sub>AsMe<sub>2</sub>)-η<sup>5</sup>-(C<sub>3</sub>Me<sub>5</sub>)]ZrCl<sub>2</sub> (**20**) in good yield. © 1997 Elsevier Science S.A.

**Keywords:** Arsenic; Boron; Cyclopentadienyl ligands; Indenyl ligands; Metallocenes; X-ray structure

### 1. Introduction

The chemistry of metallocenes is a widespread and rapidly progressing discipline. Since the discovery of ferrocene [1] an enormous number of organotransition metal complexes has been reported. At the same time, studies of the main group metallocenes reveal a lot of similarities in reactivity, bonding and structure types between main group and transition metallocenes.

The interest in modifying early transition metal complexes with main group elements as substituents is

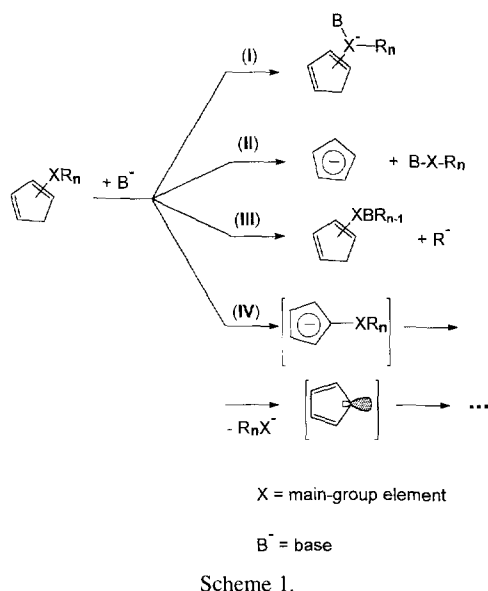
supported by the potential application of these complexes in various processes of olefin conversion and due to their further synthetic advances [2]. Our own research focusses on the coordination chemistry of main group substituted cyclopentadienyl and indenyl ligands with the early transition metals.

Here we report our results on the synthesis of polyelement substituted cyclopentadienyl and indenyl ligands bearing boron and arsenic containing groups together with some applications of these ligand precursors for the synthesis of zirconocene complexes.

Our reasons for depicting boron and arsenic were two-fold: early transition metal complexes with a boron containing substituent seem to be very important as

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<sup>1</sup> In memory of Professor Yu.T. Struchkov.



Scheme 1.

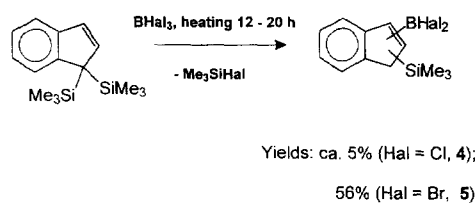
homogeneous catalysts for alkene polymerisation processes, which are a subject of great current interest [3–5]. Arsenic modified metallocenes are of potential interest as bifunctional ligand components for synthetic and structural studies of early–late heterobimetallics [6]. Therefore, it was important to develop synthetic routes towards such ligands and complexes. The standard methods including strong bases cannot be used because of the chemical lability of the boron and arsenic centres. Possible undesired side reactions are shown in Scheme 1.

## 2. Results and discussion

Different chemical and electronic effects in boron and arsenic substituted cyclopentadienes and indenenes and in complexes derived from these ligand precursors require separate discussion in the following sections.

### 2.1. Synthesis of boron containing cyclopentadienes and indenenes

Our initial attempts were concentrated on the synthesis of bis(cyclopentadienyl)phenylboranes. The choice of an aromatic substituent at boron was made due to the ability of such substituents to increase the stability and decrease the Lewis acidity of the corresponding boranes [7]. As we have found recently [8],  $PhBCp_2$  (**1**) can only be obtained by the reaction of 2 equiv. of  $CpTi$  with  $PhBCl_2$ ; lithium cyclopentadienide and its silylated analogues react with  $PhBCl_2$  exclusively to give the corresponding borates. Addition of tertiary amines to a diluted solution of  $PhBCp_2$  leads to the formation of 'B–N' adducts [8]. Only in the case of non-bulky



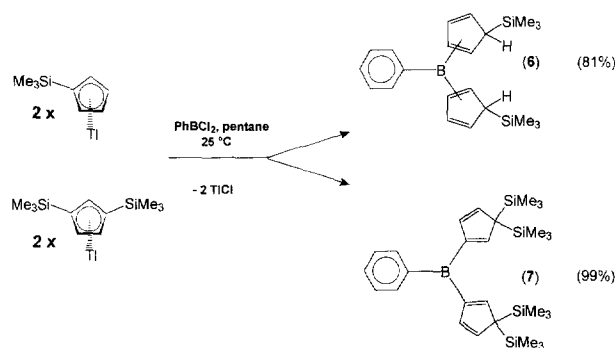
Scheme 2.

amines (e.g. pyridine and DABCO) are the adducts stable, otherwise a rapid dissociation occurs.

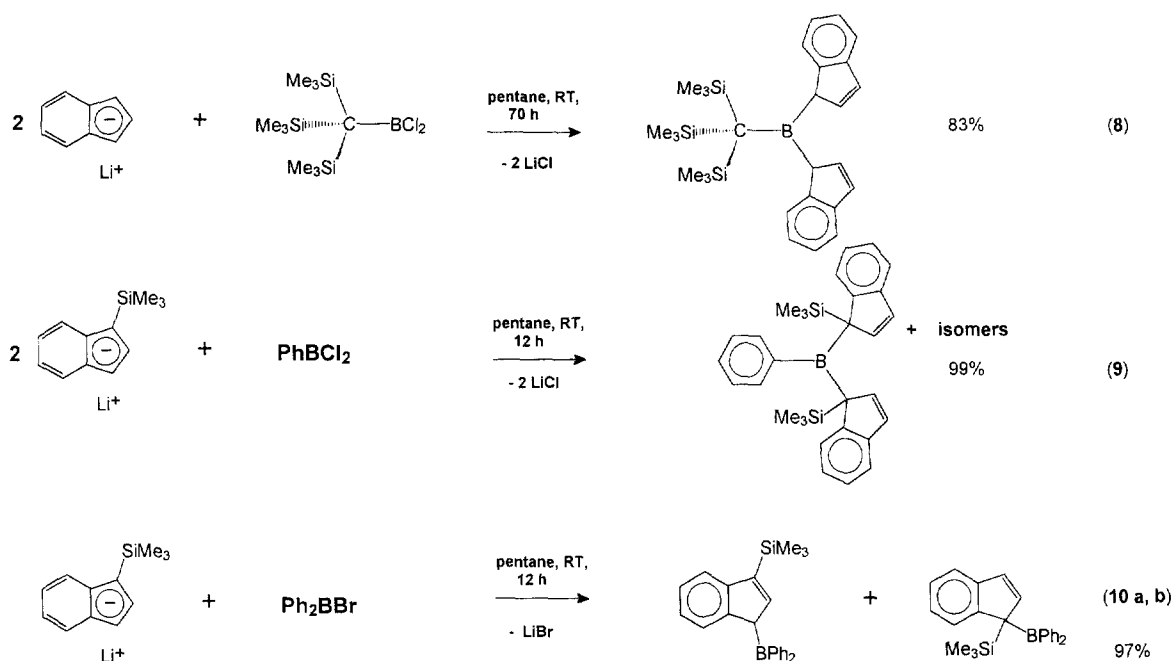
In an earlier paper Jutzi and Seufert [9] described a series of silylated cyclopentadienyl boranes. Our reinvestigation shows a similar yield for  $(C_5H_4SiMe_3)BBR_2$  (**3**) in reaction of  $Cp(SiMe_3)_2$  with  $BBr_3$  and a very moderate one for  $(C_5H_4SiMe_3)BCl_2$  (**2**) in the analogous reaction with  $BCl_3$  (see Section 4). We studied bis(trimethylsilyl)indene under similar reaction conditions since the corresponding  $Hal_2B$  substituted indenenes are expected to be more stable and therefore easier to handle (Scheme 2). All compounds discussed exist as rather complex isomeric mixtures in solution; e.g. all seven possible isomers of  $(C_9H_6SiMe_3)BBR_2$  were detected by  $^{13}C$  and  $^{29}Si$  NMR spectroscopy.

Interestingly, bis(trimethylsilyl)fluorene does not react with  $BBr_3$  at all, even under very severe reaction conditions (20 h heating at  $110^\circ C$ ). Obviously, an increase of steric hindrance at the Cp moiety prevents the Si/B exchange reaction; not unexpectedly,  $PhBCl_2$  does not react with  $Cp(SiMe_3)_2$ , even at elevated temperatures.

In contrast, thallium cyclopentadienides, which are known to be very effective transmetalating reagents [10], were shown to be useful for preparation of borylated cyclopentadienes. The reaction of  $PhBCl_2$  with  $\{Me_3SiC_5H_4\}Tl$  and  $\{(Me_3Si)_2C_5H_3\}Tl$  leads to bis(cyclopentadienyl)boranes **6** and **7** (Scheme 3). Compound **6** was obtained as a yellow–orange oil in high yield, stable at room temperature, but quickly decomposing on distillation. The  $^1H$  NMR spectrum indicates the presence of multiple isomers and a slow fluxionality of allylic  $Me_3Si$  groups. Compound **7** forms light-yel-



Scheme 3.



low crystals (from pentane) and is stable to migration in solution. Chemical shifts in the  $^{11}\text{B}$  NMR spectra are close to those of aryldivinylboranes, known from the literature [11].

For the synthesis of indenyl derivatives we applied the same strategy: substituted boron halides ( $\text{PhBCl}_2$ ,  $\text{Ph}_2\text{BBr}$  and  $(\text{Me}_3\text{Si})_3\text{C-BCl}_2$ ) were easily converted to the corresponding mono- and bis-indenyl derivatives (Scheme 4). In all compounds the boron containing substituent occupies the allylic position in the indenyl ring [12]. A broad multiplet of the allylic protons at 3.28 ppm in the  $^1\text{H}$  NMR spectrum of **8** indicates some fluxionality of the  $(\text{Me}_3\text{Si})_3\text{C-B}$  moiety. The  $^1\text{H}$  NMR spectrum of **9** is very complex due to the independent elementotropic rearrangements of  $\text{Me}_3\text{Si-}$  and  $\text{PhB}$  moieties. Indene (**10**) was obtained in high yield as a 1:1 mixture of **10a** and **10b** and also seems to be fluxional in the solution [13].

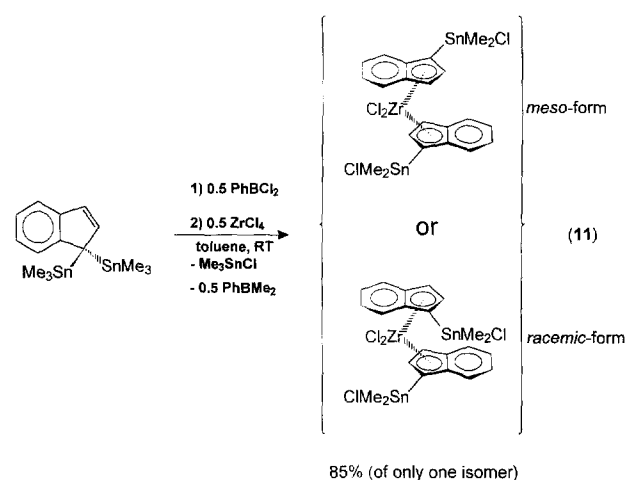
Deprotonation of the ligands described above by *t*-BuLi occurs successfully only in the case of sterically hindered bis-indene (**8**), whereas **9** and **10** undergo substitution of the indenyl fragment. Several syntheses of *ansa* and bimetallic metallocenes were described using silylated compounds as ligand precursors [14]. We found that stannylated Cp-type ligands can also be useful for these purposes.

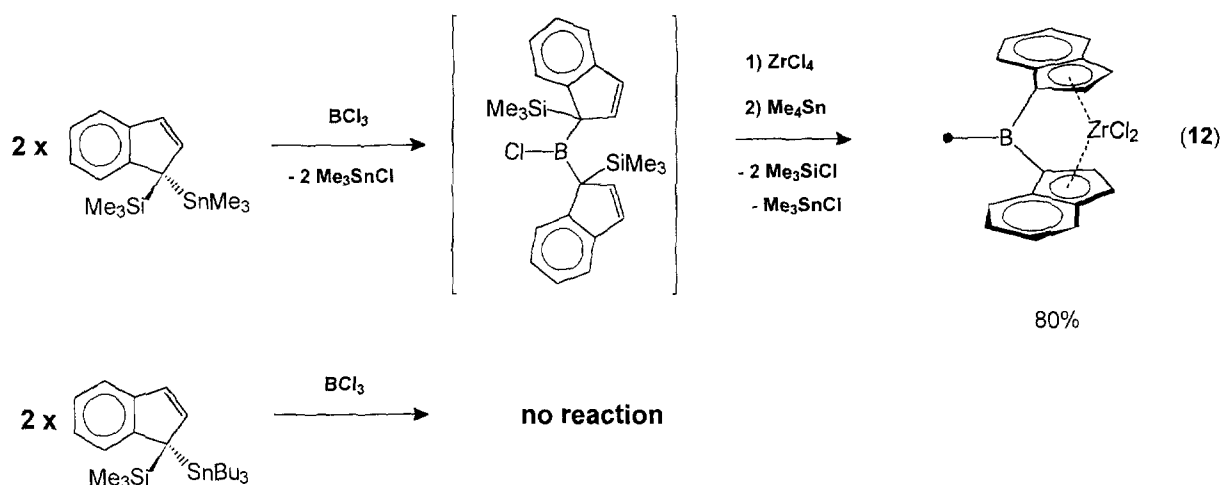
## 2.2. Borylated cyclopentadienes and indenenes as ligands for metallocene complexes

Alkali metal borylcyclopentadienides are usually difficult to obtain. Only recently some of them were

synthesised using CpNa as a base [15]. Direct metallation of borylated Cp-type ligands was described for corresponding borate species bearing one or two perfluorophenyl substituents [3]. The anions obtained were studied in reactions with Zr (Hf) tetrachlorides, but only dinuclear or simple sandwich species were detected as products. A more reliable synthetic approach to the borylated metallocenes using polymetallated ligands was briefly reported by Jutzi and Seufert [16] and recently by Reetz et al. [4]. In these reports silylated boron cyclopentadienes were applied.

Our attempts to synthesise 1,1'-boron-bridged *ansa* complexes using silylated derivatives show that the formation of bimetallic species dominates. In contrast,





the reaction of  $\text{PhB}(\text{C}_5\text{H}_4\text{SnMe}_3)_2$ , generated in situ from  $\text{PhBCl}_2$  and  $\text{Cp}(\text{SnMe}_3)_2$ , with  $\text{ZrCl}_4$  in toluene led to the desired *ansa* complex in 40% isolated yield [8]. The following experiments are aimed towards investigation of this alternative synthetic approach.

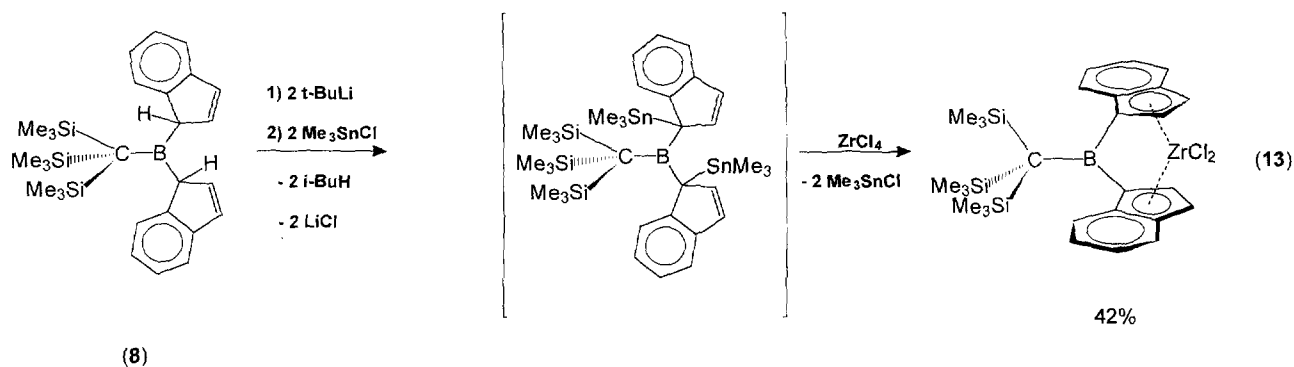
We found that the similar reaction of bis(trimethylstannyl)indene unexpectedly results in the formation of bis[ $\eta^5$ -(chlorodimethylstannyl)indenyl]zirconium dichloride (**11**) (Scheme 5).

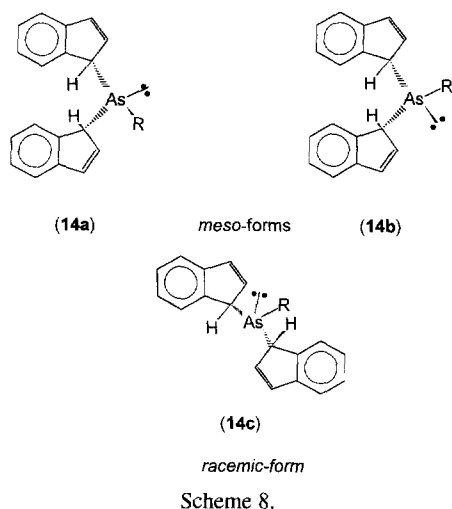
This complex is obtained in an overall yield of 85% and, as claimed on the basis of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, is present in the form of only one of two possible diastereomers. In the  $^1\text{H}$  NMR spectrum there are two singlets of diastereotopic protons at 1.25 and 0.95 ppm corresponding to the methyl groups at the tin atom, two multiplets at 6.74 and 5.98 ppm of two 'vinylic' protons indicate the presence of only one isomer. Protons of the aromatic rings comprise a complex set of multiplets of an ABCD spin-system. NMR spectra of the reaction mixture also do not indicate the presence of a second isomer. Unfortunately, a reliable assignment of the structure of the obtained diastereomer is not possible solely on the basis of NMR experiments.

(We have been unable to obtain suitable crystals for an X-ray structure determination so far, in order to establish the structure of the diastereomer. This is the subject of our current efforts.)

The above reaction opens an efficient route to halogenstannyl substituted bent metallocenes with indenyl ligands. These compounds are interesting for further derivatization of  $\text{Me}_2\text{SnCl}$  functionalities. It is noteworthy that a methyl group transfer from tin to boron is easier than that of an indenyl group, probably for steric reasons. Therefore, substitution of two chlorine atoms in  $\text{PhBCl}_2$  leads to an in situ formation of  $\text{C}_9\text{H}_6(\text{SnMe}_3)\text{SnMe}_2\text{Cl}$ . The latter undergoes smooth and selective reaction with  $\text{ZrCl}_4$ , leading exclusively to the complex **11**. Such reactions are known with silicon compounds, e.g.  $\text{Cp}(\text{SiMe}_3)\text{SiMe}_2\text{Cl}$  reacts with  $\text{ZrCl}_4$  providing  $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})_2\text{ZrCl}_2$  [17].

Boron trichloride is more electrophilic in comparison with  $\text{PhBCl}_2$ , therefore we studied the reaction of  $\text{BCl}_3$  with trialkylstannyl(trimethylsilyl)indenes. In this case the indenyl moiety is readily transferred, and bis(indenyl)boranes are formed. However, the *n*-butyl groups at tin slow down the reaction (Scheme 6).





Compound **12** was characterized by  $^1\text{H}$  NMR spectroscopy, the spectrum at room temperature consists of a complex set of multiplets in the lower field region and two singlets of the methyl protons in a 3:1 ratio, indicating the presence of two diastereomers (*rac* + *meso*). The structure of this complex is further supported by EI-MS spectrometric data. Due to its extreme moisture and air sensitivity, we failed to obtain satisfactory elemental analyses.

Finally, in the reaction of the sterically crowded bis-indene **8** with 2 equiv. of *t*-BuLi, we obtained a doubly deprotonated derivative that could be successfully transferred by subsequent transmetalation with  $\text{Me}_3\text{SnCl}$  and  $\text{ZrCl}_4$  to the boron-bridged *ansa*-zirconocene **13** in moderate yield (Scheme 7).

The structure of the complex **13** was determined by NMR spectroscopy. Assignments are based on literature data [12,13,15] and were confirmed by (H,H) COSY-45 and (H,C)-HETCOR techniques.

### 2.3. Arsenic containing indenyl ligands and their complexes

A variety of experiments was carried out with arsenic compounds of bulky cyclopentadienes, e.g. pen-

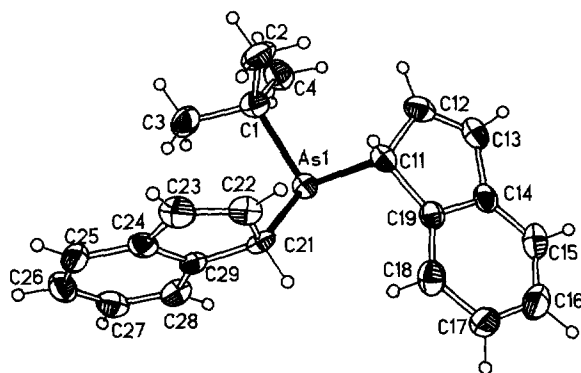


Fig. 1. ORTEP plot of **15** with atomic numbering scheme. Thermal ellipsoids are scaled to the 50% probability level.

Table 1  
Selected bond lengths (Å) and angles (°) for **15**

As(1)–C(1)	2.014(6)	C(21)–As(1)–C(11)	96.4(2)
As(1)–C(11)	2.023(5)	C(12)–C(11)–As(1)	108.6(4)
As(1)–C(21)	2.014(6)	C(19)–C(11)–As(1)	109.5(4)
		C(22)–C(21)–As(1)	117.4(4)
C(1)–As(1)–C(11)	101.5(2)	C(29)–C(21)–As(1)	112.6(4)
C(21)–As(1)–C(1)	105.2(2)		

tamethyl- or tetraisopropyl-cyclopentadiene, in order to investigate kinetically stabilised species with main group element  $\pi$ -bonds [18]. As to applications of arsenic substituted cyclopentadienyl ligands in organotransition metal chemistry, there are some reports on ferrocenyl complexes [19], but only two compounds with the early transition metals, viz.  $(\eta^5\text{-C}_5\text{H}_4\text{AsMe}_2)\text{TiCl}_3$  [20] and  $[\text{PhAs}(\eta^5\text{-C}_5\text{H}_4)_2]\text{TiCl}_2$  [21] have been reported. The main problem is the low thermal stability of arsenic cyclopentadienyls; many of these compounds decompose quickly even at temperatures well below  $0^\circ\text{C}$  [22].

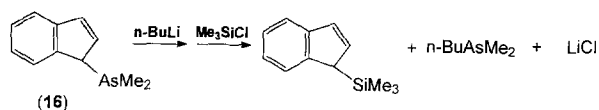
Substitution of ‘simple’ cyclopentadiene for indene increases the stability of these derivatives considerably and makes possible the synthesis and further application of such compounds as ligands in the chemistry of early transition metals.

Indenylarsenic compounds can easily be synthesised by treatment of lithiated indenenes with arsenic halides. The first compound of this series, tris(indenyl)arsane (**14**), shows the most complex structural behaviour. This

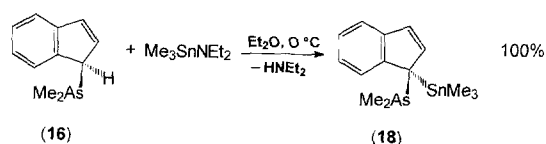
Table 2  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **15**

Atom	x	y	z	$U_{\text{eq}}$
As(1)	7829(1)	9025(1)	1703(1)	27(1)
C(1)	6849(3)	8843(4)	50(7)	34(2)
C(2)	6939(4)	9360(5)	-1469(8)	49(2)
C(3)	6016(3)	9192(5)	704(9)	52(2)
C(4)	6765(4)	7683(4)	-154(9)	45(2)
C(11)	8837(3)	9147(4)	449(7)	28(1)
C(12)	8949(4)	8151(5)	-352(8)	37(2)
C(13)	9679(4)	7691(5)	208(8)	37(2)
C(14)	10140(3)	8328(4)	1372(7)	31(2)
C(15)	10922(4)	8206(5)	2223(8)	41(2)
C(16)	11238(4)	8966(6)	3190(8)	46(2)
C(17)	10771(3)	9858(5)	3329(8)	43(2)
C(18)	9984(3)	9972(4)	2493(8)	38(2)
C(19)	9659(3)	9220(4)	1509(7)	28(1)
C(21)	7791(3)	10498(4)	2305(7)	28(1)
C(22)	7735(4)	11266(4)	1045(7)	33(2)
C(24)	6568(3)	11560(4)	2307(7)	31(2)
C(25)	5804(3)	11920(5)	2784(8)	38(2)
C(26)	5488(4)	11466(5)	4039(8)	43(2)
C(27)	5932(4)	10690(5)	4836(8)	41(2)
C(28)	6697(3)	10326(5)	4373(7)	33(2)
C(29)	7014(3)	10753(4)	3095(7)	28(2)
C(23)	7060(4)	11859(5)	1056(8)	39(2)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.



Scheme 9.



Scheme 11.

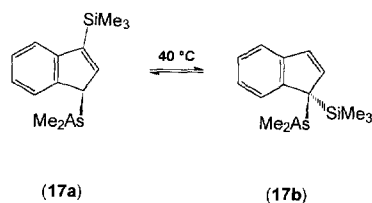
crystalline and thermally stable substance exists as a mixture of four isomers in solution. Assuming that the arsenic atom adopts an allylic position at the indenyl substituent, the situation can be described as a tris(indenyl) species composed of a bis(indenyl)arsane with a further substituent at the arsenic centre. Then there are three possible diastereomers: two *meso* forms and one *racemic* form (Scheme 8).

When a third indenyl substituent is taken into consideration this description will be changed only by an additional isomer – all three indenyl ligands are now oriented like in a *meso* form, i.e. all three allylic protons are adopting a *syn*-orientation. The other isomeric forms are of the same nature because of both *rac*- and *meso*-like oriented, pairwise separated indenyl substituents.

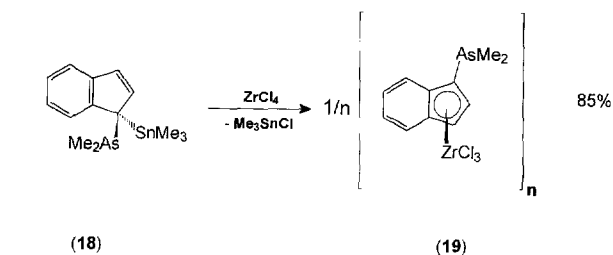
*t*-Butyl[bis(indenyl)]arsane (**15**) can be synthesised by metathesis reaction of indenyllithium with  $t\text{-BuAsCl}_2$  in moderate yield. NMR spectra of the reaction mixture indicate the presence of three diastereomers: two *meso* forms and one *racemic* form. This mixture can be separated by fractional crystallisation from *n*-hexane solution, a fraction crystallising at room temperature consists of ca. 85% of yellow crystals of the *racemic* compound and 15% of a red–orange coloured *meso* form, as confirmed by NMR spectroscopy: in the vinylic region (6.8–6.0 ppm) there are two sets of multiplets corresponding to both isomers respectively. Two resonances of the non-equivalent allylic protons of the racemate are found at 4.00 and 3.18 ppm, while only one signal at 3.87 ppm corresponds to the equivalent allylic protons of the *meso* form.

The crystal structure of the red–orange *meso* form (**15**) was determined by an X-ray crystallographic study. The molecular structure is shown in Fig. 1, important distances and angles are given in Table 1, fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

This study reveals that the red–orange coloured *meso* form of **15** presents an isomer similar to **14a** as shown in Scheme 8.



Scheme 10.



Scheme 12.

A comparison of As–C distances of two indenyl ligands reveals that they are almost identical, and with an average of 2.018(6) Å are in good agreement with the As–C distances reported for other arsenic cyclopentadienyls [22,23]. The sum of angles at the arsenic atom adds up to  $303^\circ$ , indicating a strong ‘s’-character of the lone-pair orbital at the arsenic atom. This value can be compared with  $296^\circ$  in  $\text{Cp}_3\text{As}$  [22] and is larger by  $7^\circ$ , which could be caused by steric effects.

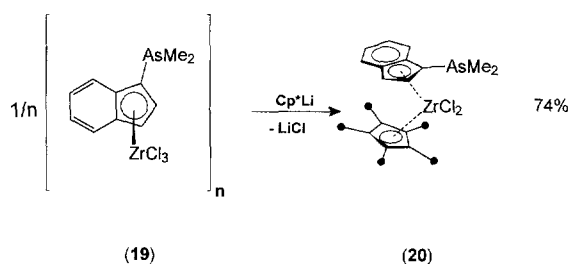
Novel indenyl arsenic compounds described here are potential ligand precursors for arsenic modified metallocenes. Some studies have been carried out using dimethylarsinoindene **16** as a model compound.

The carbon–arsenic bond in **16** is readily cleaved by treatment with  $n\text{-BuLi}$ . Mixing the reagents is immediately followed by formation of a white precipitate of lithium salt. Quenching the reaction mixture with  $\text{Me}_3\text{SiCl}$  results in the formation of trimethylsilylindene (Scheme 9).

An alternative method comprising metathesis between trimethylsilylindenyl lithium and  $\text{Me}_2\text{AsBr}$  leads to the desired product **17** in high yield, but NMR experiments showed that **17** is obtained as the only isomer with an  $\text{Me}_3\text{Si}$  group in the vinylic and an  $\text{Me}_2\text{As}$  group in the allylic position in the indenyl ring. It should be noted that for further transmetallation reactions with transition metal halides the potential leaving group ( $\text{Me}_3\text{Si}-$ ) must adopt an allylic position [20]. Attempts to convert this isomer into another one bearing the  $\text{Me}_3\text{Si}$  group in the allylic position resulted in formation of a mixture of both isomers in a 1:1 ratio (Scheme 10).

In contrast, a stannylation reaction between trimethyltin amide and **16** smoothly affords stannylated indenylarsane **18** in almost quantitative yield; in this case both substituents are bound in the allylic position (Scheme 11).

Compound **18** cannot be stored for a long time, but in situ generation followed by removal of amine makes



Scheme 13.

this method applicable for other Cp-type arsenic derivatives.

Reaction of one equivalent of **18** with  $ZrCl_4$  in toluene leads to the half-sandwich complex **19** in high yield (85%) (Scheme 12).

Interestingly,  $ZrCl_4$  does not react with two equivalents of **18** in toluene even at elevated temperatures so that exclusively **19** is formed. **19** is a bright-yellow powder, insoluble in non-polar organic solvents. With THF, DME and DMSO yellow solutions are obtained due to the formation of appropriate adducts. A bent zirconocene (**20**) can be synthesised by the reaction of **19** with 1 equiv.  $Cp^*Li$  in toluene in high yield (74%) (Scheme 13).

Compound **20** is a monomeric, crystalline solid soluble in all common organic solvents. Its structure is confirmed by analytical and spectroscopic data. It melts without decomposition and crystallises readily from toluene or etheral solutions. Further experiments on the structure and reactivity of this compound are in progress.

### 3. Conclusions

Straightforward synthetic routes to boron and arsenic cyclopentadienyl and indenyl ligand precursors for organotransition metal complexes have been developed. It was shown that simple boron and arsenic cyclopentadienyl (indenyl) ligands exist as very complex isomeric mixtures. We have found that stannylated ligands are very efficient precursors for transition metal complexes, compared with the silylated analogues.

Currently we are investigating reactions of heteroatom-bridged metallated bis-indenes with early transition metal halides as well as the application of the early transition metal amides in the synthesis of heteroelement substituted bent metallocene complexes.

### 4. Experimental section

All manipulations were performed in an atmosphere of dry, oxygen-free argon using standard Schlenk tech-

niques; solvents were appropriately dried and saturated with argon.

$n-BuLi$ ,  $t-BuLi$ ,  $Cp^*H$ ,  $AsCl_3$ ,  $BCl_3$ ,  $BBr_3$ ,  $IndH$ ,  $Me_4Sn$ ,  $Me_3SnCl$  and  $ZrCl_4$  were commercially available.

$CpSiMe_3$  [24],  $Cp(SiMe_3)_2$  [25],  $\{CpSiMe_3\}Ti$  [26],  $\{Cp(SiMe_3)_2\}Ti$  [27],  $PhBCl_2$  [28],  $Ph_2BBr$  [29],  $IndSiMe_3$  [30],  $Ind(SiMe_3)_2$  [30],  $Ind(SiMe_3)SnMe_3$  [31],  $Ind(SnMe_3)_2$  [31],  $(Me_3Si)_3CH$  [32],  $t-BuAsCl_2$  [33],  $Me_2AsBr$  [34] and  $Me_3SnNEt_2$  [35] were prepared (with minor variations) according to literature procedures.

NMR spectra were recorded on Bruker ARX 200, AC 300, AMX 500 and Varian VXR-400 spectrometers at 200, 300, 400 and 500 MHz for  $^1H$ , at 50, 75, 100 and 125 MHz for  $^{13}C$ , at 80 MHz for  $^{29}Si$  and at 96 MHz for  $^{11}B$  respectively; chemical shifts were assigned in  $\delta$  (ppm) taking the solvent as internal standard for  $^1H$  and  $^{13}C$  NMR and  $BF_3 \cdot Et_2O$  as external standard for  $^{11}B$  NMR.

Mass spectra (EI-MS) were measured on a Varian CH-7a MAT using electron impact ionisation with 70 eV excitation energy; assignments were made with reference to the most abundant isotopes.

Elemental analyses were carried out by the analytical laboratory of the Fachbereich Chemie der Philipps-Universität Marburg.

#### 4.1. Reaction of lithium trimethylsilylcyclopentadienide with phenyldichloroborane

An etheral suspension of  $(C_5H_4SiMe_3)Li$  (3.0 g, 20.4 mmol), obtained from  $n-BuLi$  and  $C_5H_5SiMe_3$ , was slowly added to 50 ml of a stirred hexane solution of  $PhBCl_2$  (1.3 ml, 10 mmol) at  $0^\circ C$ . When the addition was complete, the mixture was allowed to warm to room temperature. A white precipitate was filtered off; evaporation of the filtrate in vacuo left no product. Quenching of the white precipitate with  $D_2O$  (10 ml) and extraction of the solution with ether led, according to  $^{13}C$  NMR data (100 MHz,  $30^\circ C$ : 133.6, 127.7, 131.0) to  $PhB(OD)_2$  in low yield.

#### 4.2. (Trimethylsilylcyclopentadienyl)dichloroborane, **2**

The procedure with minor variation was similar to that described in Ref. [9].  $Cp(SiMe_3)_2$  (10.5 g, 50 mmol) was mixed with  $BCl_3$  (50 mmol, 50 ml of 1N solution in  $n$ -hexane) and the mixture was heated under reflux with an EtOH/dry ice equipped condenser for a period of 5 h. All volatiles were removed in vacuo and the residue was condensed into a Schlenk vessel cooled with liquid nitrogen at a pressure of 0.1 Torr. A light-yellow oil (7.5 g) was obtained that contained 70% of the starting  $Cp(SiMe_3)_2$  and 30% of the desired  $Cp(SiMe_3)BCl_2$ , according to  $^1H$  NMR data.

#### 4.3. (Trimethylsilylcyclopentadienyl)dibromoborane, 3

The procedure was similar to that described in Ref. [9]. The product was obtained in 62% yield as a pink viscous oil, extremely air and light sensitive. Anal. Found: C, 30.02; H, 4.22; Br, 53.0. Calc.: C, 31.21; H, 4.26; Br, 51.90%.

#### 4.4. (Trimethylsilylindenyl)dichloroborane, 4

Bis(trimethylsilyl)indene (5.21 g, 20 mmol) was mixed with 100% excess of  $\text{BCl}_3$  (40 mmol, 40 ml of 1 N solution in *n*-hexane) at room temperature. The reactants were heated under reflux with an EtOH/dry ice equipped condenser for a period of 10 h. All volatiles were removed in vacuo and the residue was condensed into a Schlenk tube cooled with liquid nitrogen at 0.05 Torr. Yield ca. 5%. As determined by NMR spectroscopy, 4 contained ca. 10% of the starting material, the bis-silylated indene.

$^1\text{H}$  NMR (300 MHz, 30°C,  $\text{C}_6\text{D}_6$ ): 8.42–8.38, 7.96–7.60 (m, m, =CH,  $\text{Ind}_{\text{vin}}$ , isomers of 4); 7.44–7.14 (m, =CH,  $\text{Ind}_{\text{Ar}}$ ); 7.05–6.95 (m, =CH,  $\text{Ind}_{\text{vin}}$ ,  $\text{Ind}(\text{SiMe}_3)_2$ ); 3.48–3.50 (m,  $\text{Ind}_{\text{All}}$ , isomers of 4); 0.45, 0.28, 0.00, –0.08, –0.13 (s, s, s, s, s,  $(\text{CH}_3)_3\text{Si}$ , isomers of 4); –0.20 (s,  $(\text{CH}_3)_3\text{Si}$ ,  $\text{Ind}(\text{SiMe}_3)_2$ ).

$^{13}\text{C}$  NMR (75 MHz, 30°C,  $\text{C}_6\text{D}_6$ , high field area): 3.1, 2.5, –0.5, –1.1, –1.5 ( $(\text{CH}_3)_3\text{Si}$ , isomers of 4); –2.7 (s,  $(\text{CH}_3)_3\text{Si}$ ,  $\text{Ind}(\text{SiMe}_3)_2$ ).

$^{11}\text{B}$  NMR (96 MHz, 30°C,  $\text{CDCl}_3$ ): 49.1.

#### 4.5. (Trimethylsilylindenyl)dibromoborane, 5

Bis(trimethylsilyl)indene (6.51 g, 25 mmol) was mixed at room temperature with  $\text{BBr}_3$  (2.83 ml, 30 mmol) without a solvent and heated to 90°C for 2 h. The dark-red mixture was dried in vacuo for 1 h to remove  $\text{Me}_3\text{SiCl}$  and excess  $\text{BBr}_3$  and finally recondensed into a Schlenk tube cooled with liquid nitrogen at 0.02 Torr. Yield 5.01 g (56%) of a light-pink oil, extremely air and light sensitive.

Anal. Found: C, 39.32; H, 3.98; Br, 45.04. Calc.: C, 40.27; H, 4.22; Br, 44.64%.

$^1\text{H}$  NMR (300 MHz, 30°C,  $\text{C}_6\text{D}_6$ ): 7.92–7.78, 7.69–7.48 (m, m, =CH,  $\text{Ind}_{\text{vin}}$ , isomers of 5); 7.28–7.09 (m, =CH,  $\text{Ind}_{\text{Ar}}$ ); 3.35–3.38 (m,  $\text{Ind}_{\text{All}}$ , isomers of 5); 0.75, 0.67, 0.32, 0.26, 0.14, 0.00, –0.10 (7 singlets,  $(\text{CH}_3)_3\text{Si}$ , isomers of 5).

$^{13}\text{C}$  NMR (75 MHz, 30°C,  $\text{C}_6\text{D}_6$ , high field area): 3.5, 3.2, 2.6, 2.2, –0.8, –1.0, –1.1 ( $(\text{CH}_3)_3\text{Si}$ , isomers of 4).

$^{11}\text{B}$  NMR (96 MHz, 30°C,  $\text{CDCl}_3$ ): 50.2.

$^{29}\text{Si}$  NMR (80 MHz, 30°C,  $\text{CDCl}_3$ ): 18.74, 9.03, 8.75, 2.87, 2.04, 1.16, –10.30 (7 different  $\text{Me}_3\text{Si}$  groups in the isomeric mixture of 5).

#### 4.6. Reaction of bis(trimethylsilyl)cyclopentadiene with phenyldichloroborane

$\text{Cp}(\text{SiMe}_3)_2$  (2.1 g, 10 mmol) was mixed with  $\text{PhBCl}_2$  (0.65 ml, 5 mmol) in heptane (15 ml). Reagents were heated under reflux, the solution turned green. According to  $^1\text{H}$  NMR monitoring of the reaction mixture no substitution occurred even after 30 h.

#### 4.7. Bis(trimethylsilylcyclopentadienyl)phenylborane, 6

$\text{PhBCl}_2$  (1 ml, 7.6 mmol) in pentane (10 ml) was added dropwise to a stirred suspension of  $(\text{CpSiMe}_3)\text{Ti}$  (5.3 g, 15.2 mmol) in pentane (80 ml), at room temperature. After 15 min a light-grey precipitate of  $\text{TiCl}$  was filtered off, the pentane solution was slowly evaporated at a temperature below 30°C to yield a bright-yellow oil, 2.23 g (81%).

$^1\text{H}$  NMR (400 MHz, 30°C,  $\text{C}_6\text{D}_6$ ): 8.32–8.08 (m, =CH, *o*-Ph, 2H); 7.92–7.74 (m, =CH,  $\text{Cp}_{\text{vin}}$ , 2H); 7.42–7.22 (m, =CH, *m*-Ph and *p*-Ph, 2H, 3H); 7.00–6.56 (br, m, =CH,  $\text{Cp}_{\text{vin}}$ , 2H); 3.57, 3.22 (t, t, >CH,  $\text{Cp}_{\text{All}}$ , 2H); –0.06, –0.11, –0.13 (s, s, s,  $\text{CH}_3\text{Si}$ , 18H).

$^{13}\text{C}$  NMR (100 MHz, 30°C,  $\text{C}_6\text{D}_6$ ): 137.15, 135.93, 128.13, 127.85, 127.57 (=CH, Ph,  $\text{Cp}_{\text{vin}}$ ); 67.80, 71.70, 45.20 (>CH,  $\text{Cp}_{\text{All}}$ ); –1.34, –2.08 (br, s, s,  $\text{CH}_3\text{-Si}$ ).

$^{11}\text{B}$  NMR (96 MHz, 25°C,  $\text{C}_6\text{D}_6$ ): 36.5.

#### 4.8. Bis(bis(trimethylsilyl)cyclopentadienyl)phenylborane, 7

12.4 g (30 mmol) of  $\{\text{Cp}(\text{SiMe}_3)_2\}\text{Ti}$  was suspended in pentane (200 ml) and 2 ml (15 mmol) of  $\text{PhBCl}_2$  was dropwise added at room temperature. The reaction mixture turned yellow; it was allowed to stir overnight. The precipitated  $\text{TiCl}$  was filtered off and washed twice with pentane (20 ml). The obtained pentane solution was slowly evaporated at a temperature below 30°C, yielding a light-yellow oil, immediately solidifying on cooling, 7.52 g (99%).

$^1\text{H}$  NMR (400 MHz, 30°C,  $\text{C}_6\text{D}_6$ ): 8.15–8.05 (m, =CH, *o*-Ph, 2H); 7.65–7.30 (m, =CH,  $\text{Cp}_{\text{vin}}$ , *m*-Ph and *p*-Ph, 2H, 3H); 6.75–6.38 (br, m, =CH,  $\text{Cp}_{\text{vin}}$ , 4H); 0.27, 0.04 (s, s,  $\text{Si}(\text{CH}_3)_3$ , 18H, 18H).

$^{13}\text{C}$  NMR (100 MHz, 30°C,  $\text{C}_6\text{D}_6$ ): 155.5, 135.9, 137.6, 135.9, 130.9 (=CH, Ph,  $\text{Cp}_{\text{vin}}$ ); 60.6 ( $\text{C}_q$ ,  $\text{Cp}_{\text{All}}$ ); 1.5, –0.4 (s, s,  $(\text{CH}_3)_3\text{-Si-Cp}_{\text{All}}$ ).

$^{11}\text{B}$  NMR (96 MHz, 25°C,  $\text{C}_6\text{D}_6$ ): 34.

#### 4.9. Tris(trimethylsilyl)methyl-diindenylborane, 8

Tris(trimethylsilyl)methane (2.25 g, 10 mmol) was mixed in hexane (100 ml) with *n*-BuLi (6.5 ml of 1.5 N solution in hexane, 10 mmol) at room temperature and



stirred for 120 h. The solution was cooled to  $-78^{\circ}\text{C}$  and  $\text{BCl}_3$  was added (10 ml of 1 N hexane solution, 10 mmol): an exothermic reaction occurred. The mixture was stirred for another hour at  $-50^{\circ}\text{C}$ , then indenyl lithium (2.35 g, 20 mmol), obtained from *n*-BuLi and indene, was added. The reaction mixture was allowed to warm to room temperature and was stirred for 70 h. The obtained solution was filtered off and evaporated under reduced pressure. Tris(trimethylsilyl)methyl-diindenylborane is a light-yellow oil, slowly crystallising in the deep freezer. Yield 3.95 g (83%). Anal. Found: C, 71.21; H, 8.59. Calc.: C, 71.15; H, 8.74%.

EI-MS (70 eV) *m/e*: 426 (76.2%,  $\text{M}^+ - 2\text{CH}_4$ ,  $-\text{CH}_3$ ); 385 (100%,  $\text{M}^+ - (\text{Me}_3\text{Si}-\text{CH}_2-)$ ); 231 (4.8%,  $(\text{Me}_3\text{Si})_3\text{C}-$ ); 115 (16.1%, Ind).

$^1\text{H}$  NMR (300 MHz,  $30^{\circ}\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 7.50–7.05, 7.02–6.85 (m, m,  $\text{Ind}_{\text{Ar}}$ ,  $\text{Ind}_{\text{vin}}$ , 8H, 2H); 3.28 (br, m,  $\text{Ind}_{\text{All}}$ , 2H); 0.16 (s,  $[(\text{CH}_3)_3\text{Si}]_3\text{C}-$ , 27H).

$^{13}\text{C}$  NMR (75 MHz,  $30^{\circ}\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 151.5 (=CH,  $\text{Ind}_{\text{vin}}$ ), 147.8, 144.5 ( $\text{C}_q$ ,  $\text{Ind}_{\text{Ar}}$ ), 126.6, 125.0, 124.0, 123.8 (=CH,  $\text{Ind}_{\text{Ar}}$ ); 41.0 ( $-\text{CH}_2-$ ,  $\text{Ind}_{\text{All}}$ ); 3.5 ( $[(\text{CH}_3)_3\text{Si}]_3\text{C}$ );  $-1.5$  ( $[(\text{CH}_3)_3\text{Si}]_3\text{C}$ ).

$^{11}\text{B}$  NMR (96 MHz,  $30^{\circ}\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 48.2.

#### 4.10. Bis(trimethylsilylindenyl)phenylborane, **9**

$\text{PhBCl}_2$  (1.69 ml, 13.0 mmol) in pentane (20 ml) was added dropwise to a stirred suspension of  $(\text{IndSiMe}_3)\text{Li}$  (5.24 g, 27 mmol), obtained from *n*-BuLi and  $\text{IndSiMe}_3$ , in pentane (80 ml), at  $-30^{\circ}\text{C}$ . After complete addition (ca. 15 min) the reaction mixture was allowed to warm to room temperature and was stirred overnight. The obtained orange mixture was filtered and the solvent was removed in vacuo, yielding **9** (6.0 g, 99%) as a bright-orange oil. Anal. Found: C, 77.56; H, 7.51. Calc.: C, 77.89; H, 7.63%.

$^1\text{H}$  NMR (300 MHz,  $30^{\circ}\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 8.12–7.94, 7.60–7.11, 7.05–6.74 (m, m, m, =CH,  $\text{Ind}_{\text{vin}}$ , Ph,  $\text{Ind}_{\text{Ar}}$ , 17H); 0.07,  $-0.04$  (s, s,  $(\text{CH}_3)_3\text{Si}$ , 18H).

$^{11}\text{B}$  NMR (96 MHz,  $30^{\circ}\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 52.8.

#### 4.11. Diphenyl(trimethylsilylindenyl)borane, **10**

$\text{Ph}_2\text{BBr}$  (12.25 g, 50.0 mmol) in hexane (100 ml) was added dropwise to a stirred suspension of  $(\text{IndSiMe}_3)\text{Li}$  (9.7 g, 50 mmol), obtained from *n*-BuLi and  $\text{IndSiMe}_3$ , in hexane (200 ml), at  $0^{\circ}\text{C}$ . After complete addition (ca. 0.5 h) the reaction mixture was allowed to warm to room temperature and was stirred overnight. The obtained orange solution was filtered off and the solvent was removed in vacuo, yielding **10** (18.50 g, 97%) as a bright-orange oil. Anal. Found: C, 81.18; H, 7.07. Calc.: C, 81.81; H, 7.15%.

$^1\text{H}$  NMR (300 MHz,  $30^{\circ}\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 7.99–7.69, 7.54–7.21, 6.97–6.59 (m, m, m, =CH, Ph,  $\text{Ind}_{\text{Ar}}$ ,  $\text{Ind}_{\text{vin}}$ ,

15H (**10a**), 16H (**10b**)); 3.41 (br, s,  $-\text{CH}$ ,  $\text{Ind}_{\text{All}}$ , 1H (**10a**)); 0.38 (s,  $(\text{CH}_3)_3\text{Si}-\text{C}_{\text{vin}}$ , 9H (**10a**)); 0.05 (s,  $(\text{CH}_3)_3\text{Si}-\text{C}_{\text{All}}$ , 9H (**10b**)).

$^{11}\text{B}$  NMR (96 MHz,  $30^{\circ}\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 61.4.

#### 4.12. Bis( $\eta^5$ -1-chlorodimethylstannylindenyl)zirconium dichloride, **11**

$\text{PhBCl}_2$  (1.82 ml, 14 mmol) was dropwise added to a toluene (150 ml) solution of  $\text{Ind}(\text{SnMe}_2)_2$  (12.37 g, 28 mmol) at room temperature under continuous stirring. The reaction mixture turned yellow. After 5 h,  $\text{ZrCl}_4$  (3.26 g, 14 mmol) was added and the mixture was allowed to stir overnight. The obtained yellow–orange solution was evaporated to dryness, washed five times with hexane (100 ml) to remove  $\text{Me}_3\text{SnCl}$  and then dried in vacuo. The crude product was recrystallised from ether, yielding 9.0 g (85%) of a bright-yellow microcrystalline powder of **11**. Anal. Found: C, 31.97; H, 4.64. Calc.: C, 34.84; H, 3.19%.

$^1\text{H}$  NMR (300 MHz,  $30^{\circ}\text{C}$ ,  $\text{CDCl}_3$ ): 7.64–7.22 (m, ABCD spin-system, 8H,  $\text{Ind}_{\text{Ar}}$ ); 6.74, 5.98 (dd, dd, 2H, 2H, =CH-,  $\text{Ind}_{\text{C5}}$ ); 1.053, 0.913 (s, s, 6H, 6H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (75 MHz,  $30^{\circ}\text{C}$ ,  $\text{CDCl}_3$ ): 131.9, 129.9 ( $\text{C}_q$ ,  $\text{Ind}_{\text{Ar}}$ ); 127.7, 126.8, 126.7, 125.3 (=CH,  $\text{Ind}_{\text{Ar}}$ ); 128.8, 105.6 (=CH,  $\text{Ind}_{\text{C5}}$ ); 1.4, 0.4 ( $\text{CH}_3$ -).

EI-MS (70 eV) *m/e*: 459 (2.67%,  $(\text{IndSnMe}_2\text{Cl})\text{ZrCl}_2$ ); 342 (2.80%,  $\text{IndMe}_2\text{SnCl}$ ); 312 (5.27%,  $\text{IndZrCl}_3$ ); 185 (56.09%,  $\text{Me}_2\text{SnCl}$ ); 115 (100%, Ind).

#### 4.13. $[(\mu\text{-Methylborilydene})\text{-bis}(\text{indenyl})]\text{zirconocene dichloride, 12}$

Trimethylsilyl(trimethylstannyl)indene (3.51 g, 10 mmol) in hexane solution was mixed at room temperature with a 1 N  $\text{BCl}_3$  hexane solution (5 ml, 5 mmol). The resulting bright-yellow mixture was stirred for 2 h, the solvent was evaporated and a suspension of  $\text{ZrCl}_4$  (1.64 g, 7 mmol) in hexane was added. Then the reaction mixture was refluxed for 2 h, evaporated to dryness and a solution of  $\text{Me}_4\text{Sn}$  (1.39 ml, 10 mmol) in 50 ml of  $\text{CH}_2\text{Cl}_2$  was added. The red–orange solution was allowed to stir overnight. The resulting solution was filtered from a small amount of an excess of  $\text{ZrCl}_4$ , the solvent was removed under reduced pressure. The residual oil was washed with hexane (10 portions of 60 ml) to remove  $\text{Me}_3\text{SnCl}$ . The solidified product was additionally dried in vacuo for 20 h. Yield 1.68 g (80%).

EI-MS: 413 (0.12%,  $\text{M}^+ - \text{H}$ ); 367 (1.16%,  $\text{CH}_2(\text{Ind})_2\text{ZrCl}$ ); 337 (1.23%,  $\text{Ind}(\text{BMe})\text{ZrCl}_3$ ); 312  $\text{IndZrCl}_3$ .

$^1\text{H}$  NMR (300 MHz,  $30^{\circ}\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ ): 7.91–7.45, 7.39–6.80 (m, m, =CH,  $\text{Ind}_{\text{Ar}}$ ,  $\text{Ind}_{\text{C5}}$ , 8H, 4H); 0.67, 0.42 (s, s,  $\text{CH}_3$ -, integral ratio 3:1, 3H).

#### 4.14. [ $\mu$ -(Tris(trimethylsilyl)methylborilydene)bis(indenyl)]zirconocene dichloride, **13**

A solution of **8** (4.55 g, 10 mmol) in a mixture of hexane (100 ml) and toluene (100 ml) was cooled to  $-78^\circ\text{C}$ , and *t*-BuLi (12.5 ml, 1.6 N solution in pentane) was slowly added with continuous stirring. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 30 h. A bright-yellow precipitate was formed, twice washed with 150 ml portions of pentane and dried in vacuo. The yield of the dilithium salt was 3.05 g (6.5 mmol, 65%). The solid was suspended in toluene (150 ml) and, on cooling with an ice-bath,  $\text{Me}_3\text{SnCl}$  (2.59 g, 13.0 mmol) was added in one portion. The mixture was stirred for 1 h at  $0^\circ\text{C}$  and  $\text{ZrCl}_4$  (1.44 g, 6.2 mmol) was added under argon overpressure. The reaction mixture was allowed to warm to room temperature with stirring overnight. The obtained solution was filtered and evaporated in vacuo. The crude solid product was washed with hexane, dried in vacuo and recrystallised from toluene. Yield 2.48 g of **13** (42% based on **8**) as a light-yellow powder.

$^1\text{H}$  NMR (500 MHz,  $0^\circ\text{C}$ ,  $\text{THF-}d_8$ ): 7.55–7.34, 7.29–7.14 (m, m, =CH,  $\text{Ind}_{\text{Ar}}$ , 8H); 6.92, 6.54 (m, m, =CH,  $\text{Ind}_{\text{CS}}$ , 2H, 2H); 0.09 (s,  $((\text{CH}_3)_3\text{Si})_3\text{C-}$ , 27H).

$^{13}\text{C}$  NMR (125 MHz,  $-75^\circ\text{C}$ ,  $\text{THF-}d_8$ ): 145.2, 144.0 ( $\text{C}_q$ ,  $\text{Ind}_{\text{Ar}}$ ); 134.7, 132.4 (=CH,  $\text{Ind}_{\text{CS}}$ ); 126.9, 124.8, 124.6, 121.2 (=CH-,  $\text{Ind}_{\text{Ar}}$ ); 0.4,  $-2.0$  ( $((\text{CH}_3)_3\text{Si-})$ ).

$^{11}\text{B}$  NMR (96 MHz,  $30^\circ\text{C}$ ,  $\text{THF-}d_8$ ): 33.2.

#### 4.15. Tris(indenyl)arsane, **14**

$\text{AsCl}_3$  (0.37 g, 2.05 mmol) in 50 ml  $\text{Et}_2\text{O}$  was slowly added to an ethereal solution of IndLi (0.76 g, 6.15 mmol), obtained from indene and *n*-BuLi in *n*-hexane, at  $-78^\circ\text{C}$ . The reaction mixture was allowed to stir for 1 h, after that it had turned to yellow. Warming to  $0^\circ\text{C}$  was followed by immediate precipitation of LiCl. The reaction mixture was stirred for another 4 h; LiCl was filtered off and a yellow, oily residue was obtained on evaporation of the solvent in vacuo. Crystallisation from hexane at  $-30^\circ\text{C}$  gave 0.79 g (1.88 mmol) of crystalline product in a yield of 92%. Anal. Found: C, 77.14; H, 5.03. Calc.: C, 75.27; H, 5.37%.

EI-MS (70 eV): 420 (0.07%,  $\text{M}^+$ ), 305 (100%,  $\text{Ind}_2\text{As}$ ), 229 (29.12%,  $\text{Ind}_2$ ), 190 (59.65%,  $\text{IndAs}$ ), 115 (64.8%, Ind).

$^1\text{H}$  NMR (300 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 7.34–6.84 (complex set of multiplets, 12H,  $\text{Ind}_{\text{Ar}}$ ), 6.62 (2m,  $\text{Ind}_{\text{vin}}$ ), 6.49 (m,  $\text{Ind}_{\text{vin}}$ ), 6.41 (m,  $\text{Ind}_{\text{vin}}$ ), 6.36 (m,  $\text{Ind}_{\text{vin}}$ ), 6.28 (m,  $\text{Ind}_{\text{vin}}$ ), 6.00 (m,  $\text{Ind}_{\text{vin}}$ ), 5.52 (m,  $\text{Ind}_{\text{vin}}$ ), overall integral intensity corresponds to 6H, 4.23 (s,  $\text{Ind}_{\text{All}}$ ), 3.80 (s,  $\text{Ind}_{\text{All}}$ ), 3.61 (s,  $\text{Ind}_{\text{All}}$ ), 3.42 (s,  $\text{Ind}_{\text{All}}$ ), 2.84 (s,  $\text{Ind}_{\text{All}}$ ), overall intensity of 3H.

$^{13}\text{C}$  NMR (75 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 145.4, 145.1 ( $\text{C}_q$ ,

$\text{Ind}_{\text{Ar}}$ ); 143.9, 143.8 ( $\text{C}_q$ ,  $\text{Ind}_{\text{Ar}}$ ); 135.9, 135.8, 135.7, 131.0, 130.9, 130.7, 130.5 (=CH,  $\text{Ind}_{\text{vin}}$ ); 126.7, 126.6, 126.4, 125.2, 125.2, 125.1, 124.9, 124.0, 123.9, 123.8, 123.5, 122.1, 121.9, 121.8, 121.7 (=CH,  $\text{Ind}_{\text{Ar}}$ ), 49.3, 48.00, 47.8, 46.5 ( $\text{C}_{\text{All}}$ ).

#### 4.16. *t*-Butyl[bis(inden-3-yl)]arsane, **15**

A solution of 1.38 g (6.85 mmol) of *t*-BuAsCl<sub>2</sub> in 20 ml  $\text{Et}_2\text{O}$  was slowly added to a solution of 1.68 g (13.7 mmol) of IndLi, obtained from indene and *n*-BuLi in *n*-hexane, in 200 ml  $\text{Et}_2\text{O}$  at  $0^\circ\text{C}$ . After complete addition the reaction mixture was stirred for 4 h and LiCl was filtered off. The solvent was removed in vacuo and the residual oil was extracted with 30 ml hexane. Yellow, well-shaped crystals of racemic form were obtained at room temperature in a yield of 43%. Another isomeric form could be obtained upon further crystallisation of the mother liquor: red–orange crystals of one meso form. Anal. Found: C, 72.56; H, 6.13. Calc.: C, 72.93; H, 6.40%.

EI-MS (70 eV) *m/e*: 362 (0.05%,  $\text{M}^+$ ), 305 (3.84%,  $\text{Ind}_2\text{As}$ ), 247 (51.29%, *t*-Bu(Ind)As), 191 (100%, IndAs), 115 (70.27%, Ind).

##### 4.16.1. Racemic form (yellow crystals)

$^1\text{H}$  NMR (300 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 7.31–7.24 (m, 2H,  $\text{Ind}_{\text{Ar}}$ ); 7.18–7.16 (m, 2H,  $\text{Ind}_{\text{Ar}}$ ); 7.14–6.95 (m, 2H,  $\text{Ind}_{\text{Ar}}$ ); 6.91–6.84 (m, 1H,  $\text{Ind}_{\text{Ar}}$ ); 6.68 (m, 2H,  $\text{Ind}_{\text{vin}}$ ); 6.64 (m, 1H,  $\text{Ind}_{\text{vin}}$ ); 6.51 (m, 1H,  $\text{Ind}_{\text{vin}}$ ); 4.00 (s, 1H,  $\text{Ind}_{\text{All}}$ ); 3.18 (s, 1H,  $\text{Ind}_{\text{All}}$ ); 0.85 (s, 9H, *t*-Bu).

$^{13}\text{C}$  NMR (75 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 146.6, 146.5, 144.1, 143.8 ( $\text{C}_q$ ); 137.3, 136.9, 130.2, 129.9 (=CH,  $\text{Ind}_{\text{vin}}$ ); 126.6, 126.1, 125.3, 124.7, 124.4, 124.3, 121.9, 121.5 (=CH,  $\text{Ind}_{\text{Ar}}$ ); 47.52, 46.7 ( $\text{C}_{\text{All}}$ ); 35.6 ( $\text{C}_q$ , *t*-Bu); 29.9 (*t*-Bu).

##### 4.16.2. Meso form (red–orange crystals)

$^1\text{H}$  NMR (300 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 7.44–7.41 (m, 2H,  $\text{Ind}_{\text{Ar}}$ ); 7.31–7.27 (m, 2H,  $\text{Ind}_{\text{Ar}}$ ); 7.24–7.05 (m, 4H,  $\text{Ind}_{\text{Ar}}$ ); 6.68 (m, 2H,  $\text{Ind}_{\text{vin}}$ ); 6.44 (m, 2H,  $\text{Ind}_{\text{vin}}$ ); 3.87 (m, 2H,  $\text{Ind}_{\text{All}}$ ); 1.18 (s, 9H, *t*-Bu).

$^{13}\text{C}$  NMR (75 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 146.1, 144.6 ( $\text{C}_q$ , Ar); 135.6, 130.3 (=CH,  $\text{Ind}_{\text{vin}}$ ); 126.5, 124.7, 124.4, 121.7 (=CH,  $\text{Ind}_{\text{Ar}}$ ); 47.7 ( $\text{C}_{\text{All}}$ ); 34.2 ( $\text{C}_q$ , *t*-Bu); 30.6 (*t*-Bu).

#### 4.17. Dimethyl(inden-3-yl)arsane, **16**

$\text{Me}_2\text{AsBr}$  (4.85 g, 26.2 mmol) was added to a diethyl ether solution of IndLi (3.2 g, 26.2 mmol), prepared from indene and *n*-BuLi in *n*-hexane. The reaction mixture was stirred for a period of 1 h at  $0^\circ\text{C}$ , then it was allowed to warm to room temperature and stirred

for another 4 h. After filtration and evaporation of the solvent a deep-yellow oil was obtained. It was purified by recondensation in vacuo on heating with a hot water bath. Yield 86%. Anal. Found: C, 59.21; H, 5.91. Calc.: C, 60.02; H, 5.95%.

EI-MS (70 eV)  $m/e$ : 220 (22.5%,  $M^+$ ), 205 (11.9%,  $M^+ - Me$ ), 115 (100%, Ind).

$^1H$  NMR (300 MHz, 25 °C,  $C_6D_6$ ): 7.36, 7.23 (d, d, 1H, 1H, Ind<sub>Ar</sub>); 7.09–7.00 (m, 2H, Ind<sub>Ar</sub>); 6.68, 6.19 (d, d, 1H, 1H, Ind<sub>Vin</sub>); 3.60 (s, 1H, Ind<sub>Ar</sub>); 0.71, 0.32 (s, s, 3H, 3H, Me).

$^{13}C$  NMR (75 MHz, 25 °C,  $C_6D_6$ ): 145.7, 143.9 ( $C_q$ , Ar); 135.1, 130.1 (=CH, Ind<sub>Vin</sub>); 126.2, 124.8, 123.0, 121.5 (=CH, Ind<sub>Ar</sub>); 47.7 ( $C_{All}$ ); 8.2, 6.2 ( $C_{Me}$ ).

#### 4.18. Dimethyl[(1-trimethylsilyl)inden-3-yl]arsane, **17a**, and dimethyl[(3-trimethylsilyl)inden-3-yl]arsane, **17b**

$Me_2AsBr$  (1.70 g, 9.2 mmol) was added to a suspension of [Ind(SiMe<sub>3</sub>)Li] (1.78 g, 9.2 mmol), prepared from IndSiMe<sub>3</sub> and *n*-BuLi in *n*-hexane, at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then allowed to warm to room temperature and to stir overnight. After filtration and evaporation of the solvent a yellow oily product was obtained in the form of isomer **17a**. Yield 94%. An isomerisation over a period of 15 h at 40 °C gave a mixture of **17a** and **17b** in a ratio of 1:1.

EI-MS (70 eV)  $m/e$ : 292 (37.32%,  $M^+$ ), 187 (39.45%,  $M^+ - Me_2As$ ), 73 (100%,  $Me_3Si$ ).

##### 4.18.1. Isomer **17a**

$^1H$  NMR (300 MHz, 25 °C,  $C_6D_6$ ): 7.54, 7.47 (d, d, 1H, 1H, Ind<sub>Ar</sub>); 7.46–7.15 (dt, 2H, Ind<sub>Ar</sub>); 6.64 (d, 1H, Ind<sub>Vin</sub>); 3.81 (s, 1H, Ind<sub>All</sub>); 0.73 (s, 3H, *MeAsMe*); 0.38 (s, 3H, *MeAsMe*); 0.31 (s, 9H,  $Me_3Si$ ).

$^{13}C$  NMR (75 MHz, 25 °C,  $C_6D_6$ ): 147.1, 146.6 ( $C_q$ , Ind<sub>Ar</sub>); 144.7 (=CH, Ind<sub>Vin</sub>); 143.0 ( $C_q$ , Ind<sub>Vin</sub>); 126.1, 125.1, 124.6, 123.1, 122.5 (=CH, Ind<sub>Ar</sub>); 49.0 ( $C_{All}$ ); 8.5 ( $C_{Me}$ , *MeAsMe*); 6.1 ( $C_{Me}$ , *MeAsMe*).

##### 4.18.2. Isomer **17b**

$^1H$  NMR (300 MHz, 25 °C,  $C_6D_6$ ): 7.51–7.48 (dd, 2H, Ind<sub>Ar</sub>); 7.24–7.17 (dt, 2H, Ind<sub>Ar</sub>); 6.92, 6.39 (d, d, 1H, 1H, Ind<sub>Vin</sub>); 0.80 (s, 3H, *MeAsMe*); 0.18 (s, 3H, *MeAsMe*); –0.01 (s, 9H,  $Me_3Si$ ).

$^{13}C$  NMR (75 MHz, 25 °C,  $C_6D_6$ ): 147.2, 140.8 ( $C_q$ , Ind<sub>Ar</sub>); 136.9, 128.8 (=CH, Ind<sub>Vin</sub>); 124.7, 123.9, 122.5, 121.3 (=CH, Ind<sub>Ar</sub>); 67.5 ( $C_q$ , Ind<sub>All</sub>); 8.6 ( $C_{Me}$ , *MeAsMe*); 5.6 ( $C_{Me}$ , *MeAsMe*); –2.1 ( $Me_3Si$ ).

#### 4.19. Dimethyl[(3-trimethylstannyl)inden-3-yl]arsane, **18**

$Me_3SnNEt_2$  (0.47 g, 2.0 mmol) was added to a solution of **16** (0.44 g, 2.0 mmol) in 50 ml Et<sub>2</sub>O at 0 °C. The

reaction mixture was stirred for 1 h at 0 °C and all volatiles were removed in vacuo. A yellow oil was obtained in nearly quantitative yield.

EI-MS (70 eV)  $m/e$ : 220 (23.7%,  $Me_2AsInd$ ), 205 (11.2%,  $MeAsInd$ ), 163 (1.2%,  $Me_3Sn$ ), 114 (100%, Ind).

$^1H$  NMR (300 MHz, 25 °C,  $C_6D_6$ ): 7.67, 7.54 (m, m, 1H, 1H, Ind<sub>Ar</sub>); 7.23–7.18 (m, 2H, Ind<sub>Ar</sub>), 7.00, 6.60 (d, d, 1H, 1H, Ind<sub>Vin</sub>); 0.93 (s, 3H, *MeAsMe*); 0.38 (s, 3H, *MeAsMe*); 0.00 (s, 9H,  $Me_3Sn$ ,  $^2J(^{119}Sn-^1H) = 52.9$  Hz).

$^{13}C$  NMR (75 MHz, 25 °C,  $C_6D_6$ ): 149.1, 143.1 ( $C_q$ , Ind<sub>Ar</sub>); 137.3 (=CH, Ind<sub>Vin</sub>,  $^2J(^{119}Sn-^{13}C) = 21.9$  Hz); 126.7 (=CH, Ind<sub>Vin</sub>); 124.3, 123.9, 121.8, 121.4 (=CH, Ind<sub>Ar</sub>); 48.4 ( $C_q$ , Ind<sub>All</sub>); 8.6 ( $C_{Me}$ , *MeAsMe*); 6.0 ( $C_{Me}$ , *MeAsMe*); –8.8 ( $Me_3Sn$ ,  $^1J(^{119}Sn-^{13}C) = 91.5$  Hz).

#### 4.20. $\eta^5$ -(Dimethylarsino)indenylzirconium trichloride, **19**

ZrCl<sub>4</sub> (1.74 g, 7.5 mmol) was added to a stirred solution of **18** (7.5 mmol), prepared in situ as described in Section 4.19, at 0 °C. The reaction mixture turned bright-yellow, whereby a yellow, insoluble precipitate began to form. This suspension was allowed to stir at room temperature for another two days. After washing the precipitate with hexane to remove  $Me_3SnCl$ , the obtained microcrystalline yellow powder was dried in vacuo. Yield 85% (2.63 g). Anal. Found: C, 30.97; H, 3.18. Calc.: C, 31.71; H, 2.90%.

EI-MS (70 eV)  $m/e$ : 311 (2.1%,  $M^+ - AsMe_2$ ), 232 (12%, ZrCl<sub>4</sub>), 219 (42%, IndAsMe<sub>2</sub>), 114 (100%, Ind).

$^1H$  NMR (300 MHz, 25 °C, DMSO-*d*<sub>6</sub>): 7.35–7.21 (m, 2H, Ind<sub>Ar</sub>); 7.14–7.01 (m, 3H, Ind<sub>Ar</sub> + Ind<sub>C5</sub>); 6.52 (m, 1H, Ind<sub>C5</sub>); 1.09 (s, 3H, *MeAsMe*); 0.86 (s, 3H, *MeAsMe*).

#### 4.21. $\eta^5$ -(Dimethylarsino)indenyl- $\eta^5$ -pentamethylcyclopentadienyl-zirconium dichloride, **20**

A suspension of 0.98 mmol Cp\*Li, prepared by the reaction of Cp\*H with *n*-BuLi in toluene, was added to a suspension of 0.41 g (0.98 mmol) **19** in toluene at 0 °C. The reaction mixture was stirred for 20 min at this temperature and then allowed to warm to room temperature and to stir overnight. After filtration and evaporation of the solvent a yellow, crystalline powder was obtained. The crude product was washed twice with hexane and dried in vacuo. Yield 74%. Anal. Found: C, 47.91; H, 5.38. Calc.: C, 48.84; H, 5.27%.

EI-MS (70 eV)  $m/e$ : 516 (4.9%,  $M^+$ ), 501 (4.1%,  $M^+ - Me$ ), 295 (24.4%, Cp\*ZrCl<sub>2</sub>), 115 (100%, Ind).

$^1H$  NMR (300 MHz, 25 °C,  $C_6D_6$ ): 7.83, 7.18 (m, m, 1H, 1H, Ind<sub>Ar</sub>); 7.00–6.96 (m, 2H, Ind<sub>Ar</sub>); 5.91, 5.75

(m, m, 1H, 1H, Ind<sub>C5</sub>); 1.70 (s, 15H, Cp<sup>\*</sup>); 1.07 (s, 3H, MeAsMe); 1.04 (s, 3H, MeAsMe).

<sup>13</sup>C NMR (75 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>): 144.1, 142 (C<sub>q</sub>, Ind<sub>Ar</sub>); 132.0 (C<sub>q</sub>, Cp<sup>\*</sup>); 127.1, 126.2, 125.9, 124.8 (=CH, Ind<sub>Ar</sub>); 121.5 (C<sub>q</sub>, =CAsMe<sub>2</sub>, Ind<sub>C5</sub>); 119.3, 101.5 (=CH, Ind<sub>C5</sub>); 12.6 (C<sub>Me</sub>, Cp<sup>\*</sup>); 11.0 (C<sub>Me</sub>, MeAsMe); 9.9 (C<sub>Me</sub>, MeAsMe).

#### 4.22. X-ray crystal study of 15

A small crystal of dimensions 0.14 × 0.10 × 0.10 mm<sup>3</sup> was placed in a glass capillary and mounted on a Siemens-P4 four-circle diffractometer. Data were collected using ω-scans, Mo Kα radiation (0.71073 Å): monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 15.672(4), *b* = 13.176(4), *c* = 8.766(1) Å, β = 95.94(2)°; *V* = 1800.5(7) Å<sup>3</sup>; *Z* = 4; *D*<sub>c</sub> = 1.299 g cm<sup>-3</sup>; μ = 1.884 mm<sup>-1</sup>; 2.02° < θ < 23.00°; *wR*<sub>2</sub> (all data on *F*<sup>2</sup>) = 0.1074, *R*<sub>1</sub> = 0.0472 for 1687 reflections with *F* > 46σ(*F*) (unique data 2513). The structure was solved by direct methods using the SHELXS-96 programme [36] and refined by a full-matrix least-squares procedure with SHELXL-96 [37]. All non-hydrogen atoms were refined anisotropically. After a semi-empirical absorption correction the locations of all hydrogen atoms were determined using a difference Fourier map and refined in a riding model. Detailed crystallographic results are obtainable from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, on specifying the depository number CSD-405784, the names of the authors and the journal reference.

#### Acknowledgements

Support of this work was provided by the Russian Foundation of Basic Research under Grant No. 96-03-34231a and by ISSF (JAG-100). K.R. and D.L. thank the Government of Hessen (Germany) for financial support (HSP-II-Programm) over the period of their research at the Philipps-Universität Marburg. Support by the Graduierten-Kolleg "Metallorganische Chemie" of the Philipps-Universität Marburg (a doctoral fellowship for E.A.) and by the Fonds der Deutschen Chemischen Industrie VCI (for J.L.) is gratefully acknowledged.

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